

Study of Local Magnetic Properties of an Adsorbate by Spin-Polarized Auger-Electron Spectroscopy

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The spin-polarized sulfur $L_{2,3}VV$ Auger spectrum is recorded for the system $c(2\times 2)\text{S}/\text{Fe}(001)$. Convolution of the calculated spin-dependent projected local density of states gives good agreement with the measured spectrum. As in previous studies a strong satellite is observed in the Auger spectrum and this is shown to be due to the presence of hybridized iron states at the sulfur site. The spectrum also shows an exchange splitting of 0.2 eV in reasonable agreement with the calculation. The integrated spin-up and spin-down Auger intensity gives an estimate of the magnetic moment of the sulfur adsorbate, $\leq 0.10\mu_B$.

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In recent years spin-polarized electron spectroscopies have contributed much to the understanding of magnetic behavior at surfaces and interfaces.¹ One technique is spin-polarized Auger-electron spectroscopy (SPAES), which has previously been demonstrated for both Fe in a ferromagnetic spin-glass system² and also oxygen from an oxidized Fe surface.³ This technique has further been shown to be capable of providing important information on local magnetic properties, as, for example, on the relative orientation of the magnetic moments in multiautomic systems.⁴ Aside from these magnetic studies there have been several investigations of the role of interatomic versus intra-atomic transitions in the Auger decay of core holes. By comparing the Auger spectra of a given atom in different environments it has previously been suggested that interatomic transitions may be responsible for the fine structure observed in these spectra.⁵

In this paper we apply the technique of SPAES to a well defined overlayer system. Our results demonstrate that it is possible to obtain detailed information on the spin-dependent total density of states of an adsorbate, measure the average exchange splitting, and hence also provide an estimate of the magnetic moment of an adsorbate atom. Further, by comparing with first-principles calculations we are clearly able to identify that component of the spectrum that represents the involvement of the substrate electrons.

We have studied the $c(2\times 2)\text{S}/\text{Fe}(001)$ adsorbate system by measuring the spin-polarized sulfur $L_{2,3}VV$ Auger-electron emission. The surface and electronic structure of this system have been previously studied by both low-energy electron diffraction⁶ and angle-resolved photoemission.⁷ Very recently, angle-resolved, spin-polarized photoemission experiments⁸ together with first-principles spin-polarized calculations⁹ have explored the magnetic properties of this system.

The spin-polarized Auger-electron experiments were performed using a 2-keV electron beam as the primary excitation source. The angle of incidence of this beam

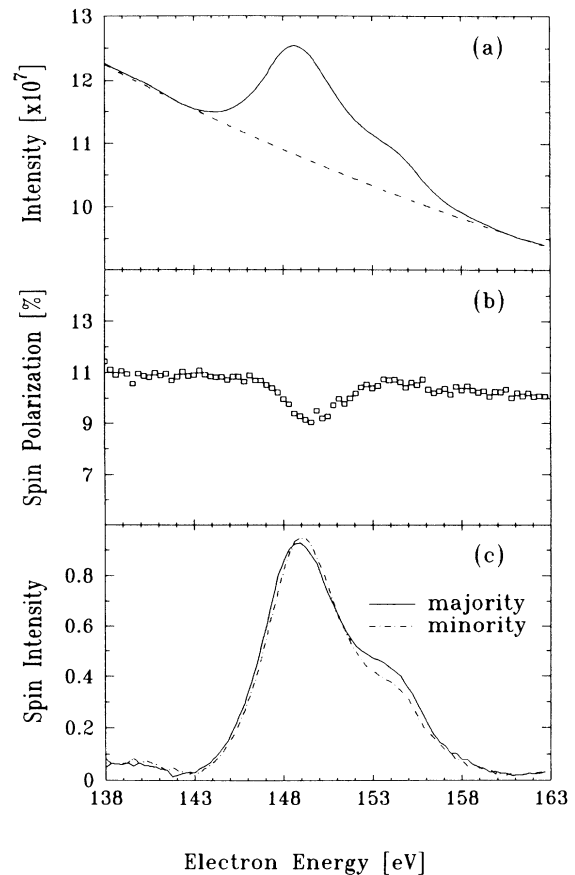


FIG. 1. Spin-polarized sulfur $L_{2,3}VV$ Auger spectrum taken from the $c(2\times 2)\text{S}/\text{Fe}(001)$ system. (a) Spin-integrated Auger spectrum (---, secondary electron background); (b) spin polarization in the Auger spectrum; (c) spin-resolved sulfur $L_{2,3}VV$ Auger spectra (—, majority spin electrons; ---, minority spin electrons) with the secondary electron background removed. The percentage error in the spin polarization shown in (b), $\pm 0.15\%$, is indicated approximately by the dimension of the squares.

was chosen to be 45° . The spin, energy, and angle of emission of the sulfur $L_{2,3}VV$ Auger electrons have been measured in a new apparatus, which has previously been used for our earlier photoemission study of the same system.⁸ Briefly the electrons are collected by a hemispherical analyzer and spin analyzed by a compact low-energy spin detector.¹⁰ The complete apparatus will be described in detail elsewhere.¹¹ The energy resolution was of the order of 0.25 eV and the angular resolution was $\pm 15^\circ$. The $c(2\times 2)$ S overlayer structure was obtained by segregation from the bulk.

In Figs. 1(a) and 1(b), we show the angle-integrated sulfur $L_{2,3}VV$ Auger spectrum from a $c(2\times 2)$ S/Fe(001) surface and the measured spin polarization of the electrons within that spectrum. The electrons were detected in an angle-resolving instrument and thus the spectrum shown in the figure is the sum of eighteen individual spectra obtained by rotating the analyzer in the (001) plane of the crystal. The polar angles of these spectra range from -30° to $+35^\circ$ with respect to the surface normal. The individual spectra have similar line shapes, the only difference being their relative intensities, a reflection of electron diffraction effects.¹² The sulfur Auger spectrum agrees well with a previous study⁵ in that there is a broad (FWHM ~ 4.0 eV) main peak and a strong shoulder observed at ~ 5 eV higher kinetic energy. The shoulder has approximately the same width as the main peak. In Fig. 1(c) we show the spin-resolved spectra obtained by folding the spin polarization back into the Auger spectrum of Fig. 1(a) using standard methods¹ and subtracting appropriate backgrounds. An identical form was used for the background in the two spin components.¹³

An Auger spectrum involving an initial core hole and two valence electrons may be described, to first approximation, by the self-convolution of the occupied density of

states (DOS) in the valence band. Chubb and Pickett⁹ have carried out a first-principles calculation of the electronic structure of the $c(2\times 2)$ S/Fe system. In Fig. 2 we show their spin-separated projected local DOS on the sulfur site. In Fig. 3 we show the self-convolution of this DOS. In that the Coulomb matrix element for the Auger transition contains no spin dependence and also that the initial core hole is not spin polarized, this self-convolution in Fig. 3 is obtained using

$$I_{\uparrow}(E) = \int_{-\infty}^{E_F} n_{\uparrow}(\epsilon) n_{\uparrow}(\epsilon - E) d\epsilon + \int_{-\infty}^{E_F} n_{\downarrow}(\epsilon) n_{\downarrow}(\epsilon - E) d\epsilon$$

and

$$I_{\downarrow}(E) = \int_{-\infty}^{E_F} n_{\uparrow}(\epsilon) n_{\downarrow}(\epsilon - E) d\epsilon + \int_{-\infty}^{E_F} n_{\downarrow}(\epsilon) n_{\uparrow}(\epsilon - E) d\epsilon,$$

where n_{\uparrow} and n_{\downarrow} are the spin-dependent densities of states from Fig. 2. It will be seen that good agreement is obtained in overall shape between the experimental Auger spectrum in Fig. 1(c) and the self-convolution of the local DOS in Fig. 3. Our interpretation of the sulfur Auger spectrum is therefore that the main peak is effectively due to the self-convolution of the "pure" sulfur DOS while the shoulder reflects the bonding to the substrate. The latter results from the presence of Fe d hybridized orbitals within the sulfur "muffin tin" and these participate in the decay of the sulfur core hole. The self-convolution of the DOS for a layer of sulfur atoms separated from the Fe substrate results in a single symmetric peak closely resembling the sulfur Auger spectrum with no shoulder. The Fe $3d$ electrons involved in the Auger process are not fully localized within the adjacent muffin tins and hence do not represent true "interatomic" transitions. They are, however, hybridized orbitals involved in the bonding with components in both substrate and adsorbate muffin tins. In the terminology of Fuggle, the shoulder therefore reflects the "multisite orbital" Auger transition.¹⁴

Closer inspection of Fig. 3 shows that the relative sep-

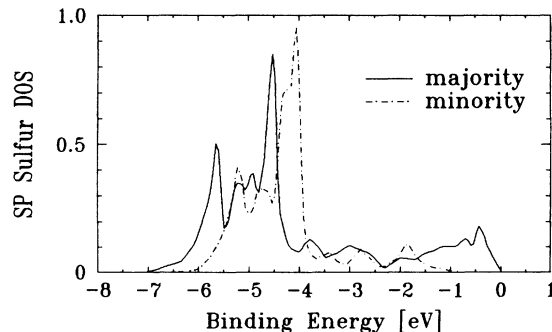


FIG. 2. Calculated local density of states on the sulfur site for the $c(2\times 2)$ S/Fe(001) system (from Ref. 9). The majority spin density (—) and minority spin density (---) are exchange split by ~ 0.5 eV. The intense feature below -4 eV is due primarily to the valence S $3p$ orbitals, and the background extending up to E_F is due to Fe $3d$ orbitals; inclusion of this background is crucial for our model for the satellite.

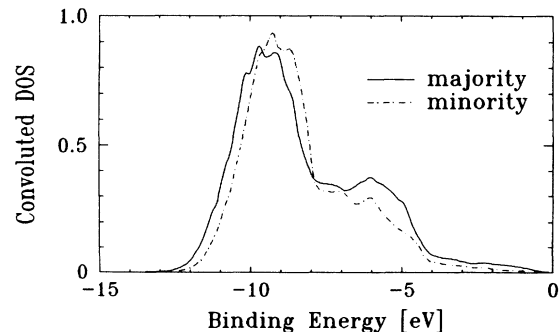


FIG. 3. Spin-dependent convolution of the calculated (Ref. 9) sulfur density of states (DOS) in Fig. 2. Convolution of the majority DOS with the total DOS (—) and the convolution of the minority DOS with the total DOS (---).

aration of the main peak and shoulder is less than that observed experimentally. It is uncertain whether this reflects an incorrect description of the ground state or a final-state effect, the former resulting from errors in the calculation, the latter from the excitation process. Artificially increasing the binding energy of the S $3p$ level by 1.0 eV brings the model into complete agreement with the experiment.¹⁵ Interestingly, the self-convolution of the local DOS has been carried out with complete neglect of any possible difference in the relative matrix elements for the Auger process involving either sulfur $3p$ electrons or the substrate $3d$ electrons. Indeed this suggests that such effects are unimportant for these levels and probably reflects the fact that within the sulfur muffin tin the substrate component will have the same symmetry as the $3p$ orbitals with which they hybridize.

An alternative explanation of the Auger line shape is the possibility that the Auger decay for adsorbed sulfur is dominated by quasiautomatic processes.¹⁴ The spin-polarized Fe core-core-core Auger spectrum from a ferromagnetic glass has indeed previously been explained in the atomic limit.² In this picture the main peak represents the singlet two-hole final state and the shoulder represents the triplet final state. However, this model is ruled out through the observation that the main peak displays an exchange splitting—in the atomic picture the singlet peak would show no polarization and no exchange splitting.

Examination of Fig. 1(c) shows that the two spin components are split in energy by 0.2 ± 0.02 eV, where the error is due to the error in the Sherman function of the spin detector.¹¹ The splitting is a direct reflection of the exchange splitting of the adsorbate-derived valence bands participating in the Auger process and, as in our earlier photoemission study,⁸ is evidence of a small magnetic moment on the adsorbate. It should be noted that any exchange splitting of the initial core hole will not result in an exchange splitting of the emitted Auger electrons. With no spin dependence in the Auger deexcitation process such a splitting would only result in equal broadening of both the majority and minority Auger components. For the first time, therefore, the present results demonstrate that spin-polarized Auger-electron spectroscopy can directly measure an average local exchange splitting on an atom. Further, the observation of the majority spectrum at a higher binding energy than the minority component is clear and direct evidence for the sulfur magnetic moment being aligned parallel to the substrate Fe moments. Aside from the exchange splitting the largest polarization effects are observed in the region of the shoulder. This is again confirmation of the involvement of the substrate d electrons in the Auger decay. The observation of a positive net polarization within the shoulder further confirms the alignment of the sulfur magnetic moment and the moments on the neigh-

boring iron atoms involved in the bonding.

In Fig. 1(c) the ratio of the integrated spin-up to spin-down intensity is 1.046. This ratio is directly proportional to the ratio of spin-up to spin-down electrons within the valence band. This quantity can therefore be used to calculate the magnetic moment on the sulfur atom, provided that the total number of electrons on that site is known. We estimate the total valence charge within the sulfur muffin tin by first assuming that the total (occupied plus unoccupied) DOS of sulfur amounts to 6.0 electrons. The occupied fraction of the calculated DOS is then equivalent to 4.3 electrons which produces an estimate for the magnetic moment of the sulfur atom of $0.10\mu_B$. This value is in good agreement with the calculation¹⁶ which estimates the magnetic moment to be less than $0.10\mu_B$. It can be further argued that our estimate provides a maximum value for the magnetic moment. This follows from the observation that the Auger process is governed by the Coulomb interaction so that the relevant scale is the radial distribution of the initial core hole. In the case studied here, the appropriate core level, the S $2p$ orbital, has maximum radial distribution at 0.3 Å.¹⁷ Comparing this with the muffin-tin radius of 0.77 Å used in the calculation suggests that the number of electrons involved in the Auger process will be less than the total number of electrons inside the muffin-tin sphere. Assuming that there is no change in the ratio of majority to minority electrons throughout the muffin tin, our work provides an upper estimate on the value of the magnetic moment.

In summary, the present work provides clear evidence that the sulfur $L_{2,3}VV$ Auger spectrum measured for the $c(2 \times 2)$ S/Fe(001) system has a component containing transitions involving multisite valence orbitals. These transitions, however, do not represent true interatomic processes in the sense that the electrons involved are contained inside the muffin tin of a single atom. Spin-polarized Auger-electron spectroscopy has been shown to be capable of measuring an average local exchange splitting in the valence band. This implies the existence of a magnetic moment on the atom being studied and further gives the direction of this moment with respect to the direction of the magnetizing field. Finally, an estimate of the magnetic moment of the adsorbate has been made from the integrated majority and minority Auger intensities. This value, $\leq 0.1\mu_B$, is in good agreement with the calculated value.

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¹³Different functional forms of the background have given essentially the same results. Indeed the shift between the majority and minority Auger spectra differs by only 0.02 eV when a linear background is used rather than an inverse dependence.

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